

Time Resolved X-ray Diffraction and Non-thermal inelastic X-ray Scattering

P. Sondhauss, M. Harbst, O. Synnergren, J. Larsson
MAX-lab, Lund University, Sweden

A. Plech, G.A. Naylor, K. Scheidt, M. Wulff
ID9 @ ESRF, Grenoble, France

J.S. Wark
Clarendon Lab, University of Oxford, UK

TRXD — how do phonons affect X-ray diffraction?

Wave picture

phonon creates periodic superstructure

⇒ grating

⇒ grating diffraction orders add to rocking curve (lattice diffraction)

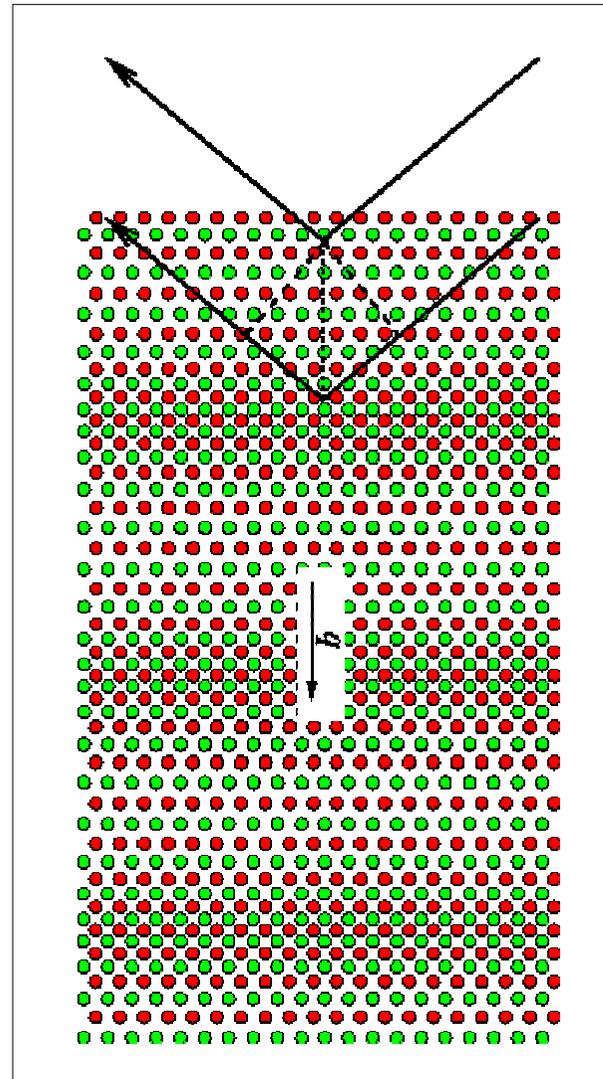
Modified *Laue condition*

$$k_s = k \pm q + G$$

Inelastic due to Doppler effect (phonon grating moves w. speed of sound)

$$\omega_s = \omega \pm m\Omega$$

m : grating diffraction order



TRXD — how do phonons affect X-ray diffraction?

particle picture

conservation of energy and momentum

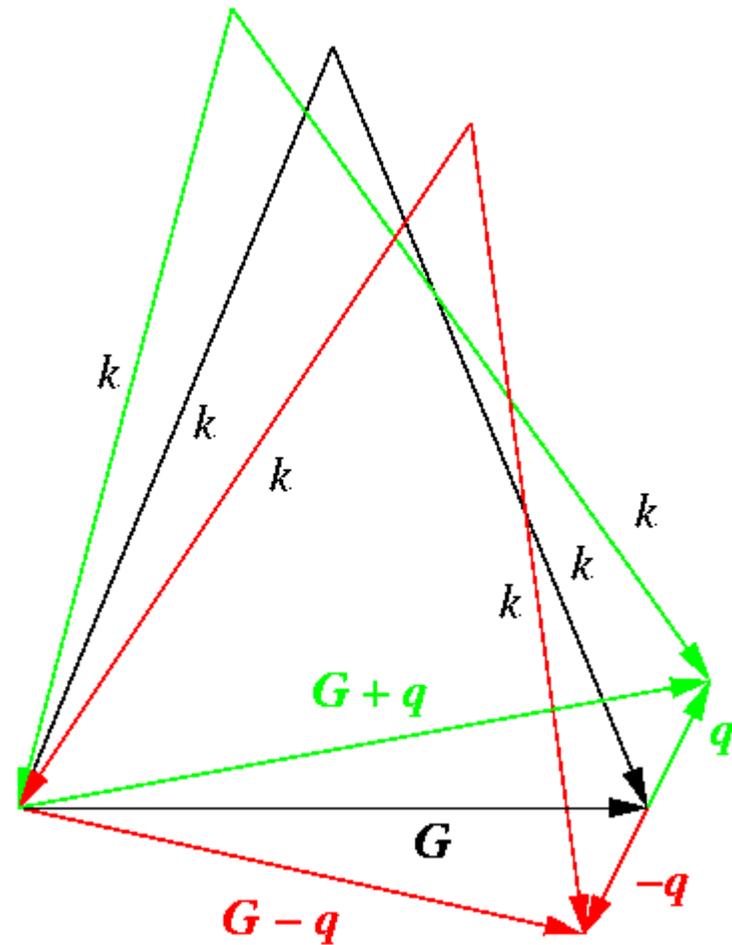
$$\hbar \omega_s = \hbar \omega \pm \hbar \Omega$$

$$\hbar \mathbf{k}_s = \hbar \mathbf{k} \pm \hbar \mathbf{q} + \hbar \mathbf{G}$$

$$\omega \sim \Omega$$

⇒ pseudo elastic

$$\mathbf{k}_s = \mathbf{k}$$



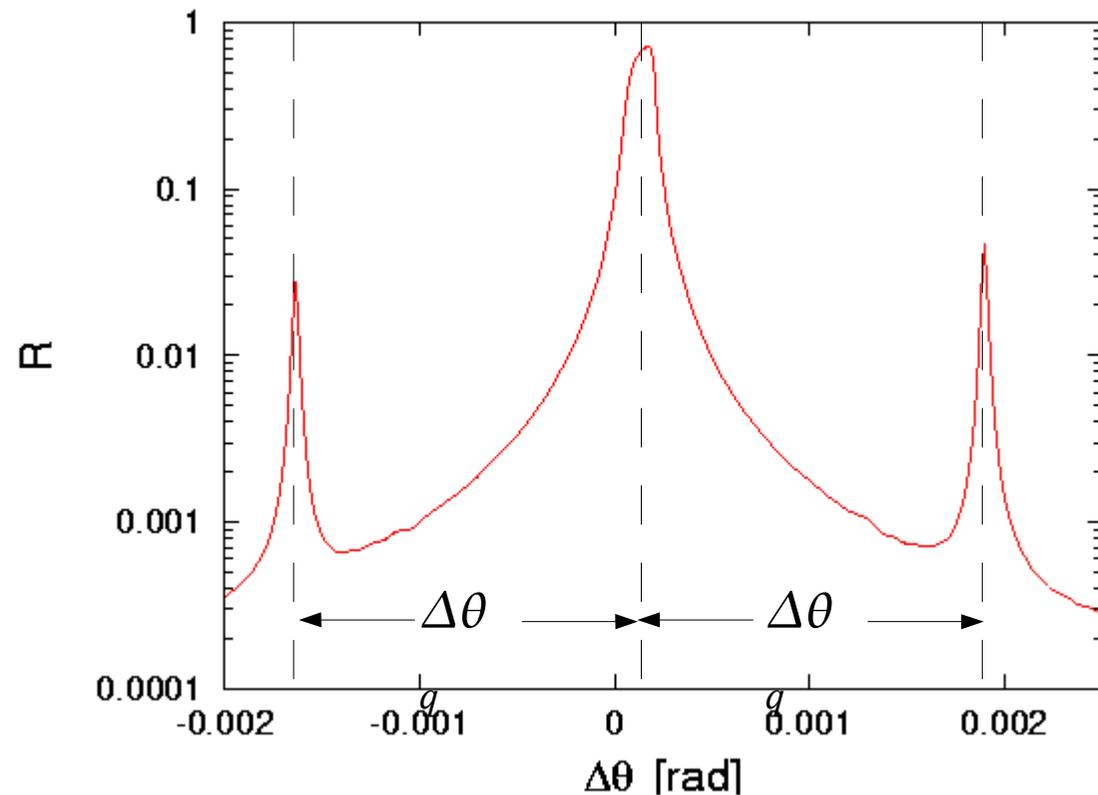
Effects of phonons on the rocking curve

single mode phonons ...

... with wavevector q generate side-bands to the rocking curve
@

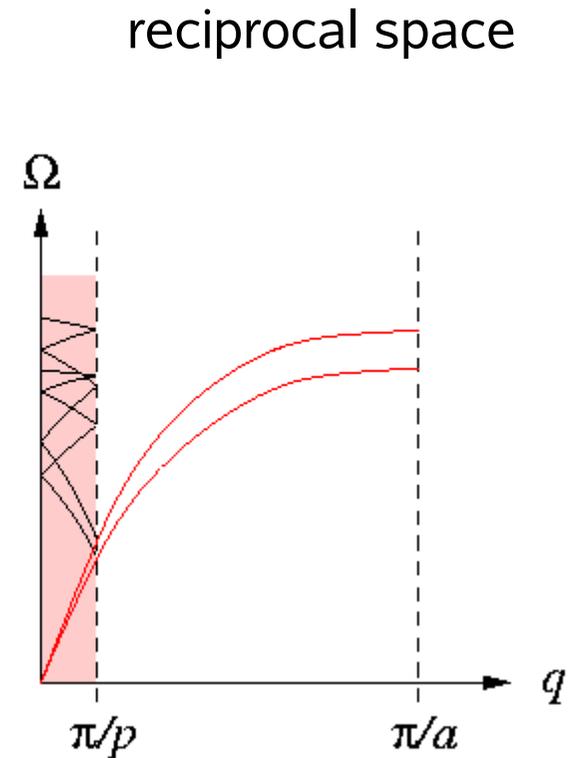
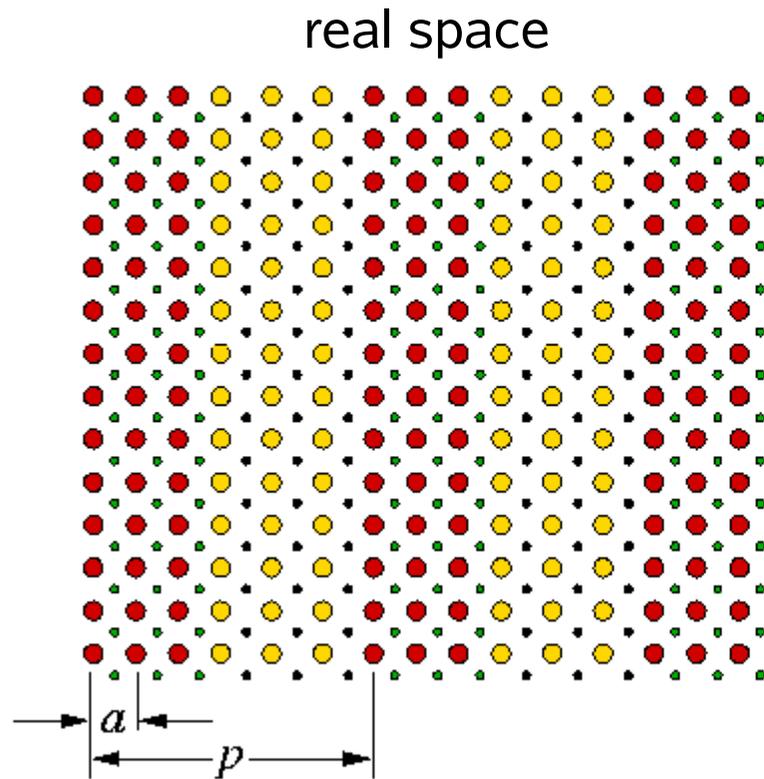
$$\frac{\Delta\Theta_q}{\tan\Theta_B} = \frac{q}{G}$$

if $q \parallel G$



- measuring R at a single point on the rocking curve selects phonon wavevector q
- for *coherent phonons* sidebands oscillate with Ω_q

Acoustic phonons in superlattices

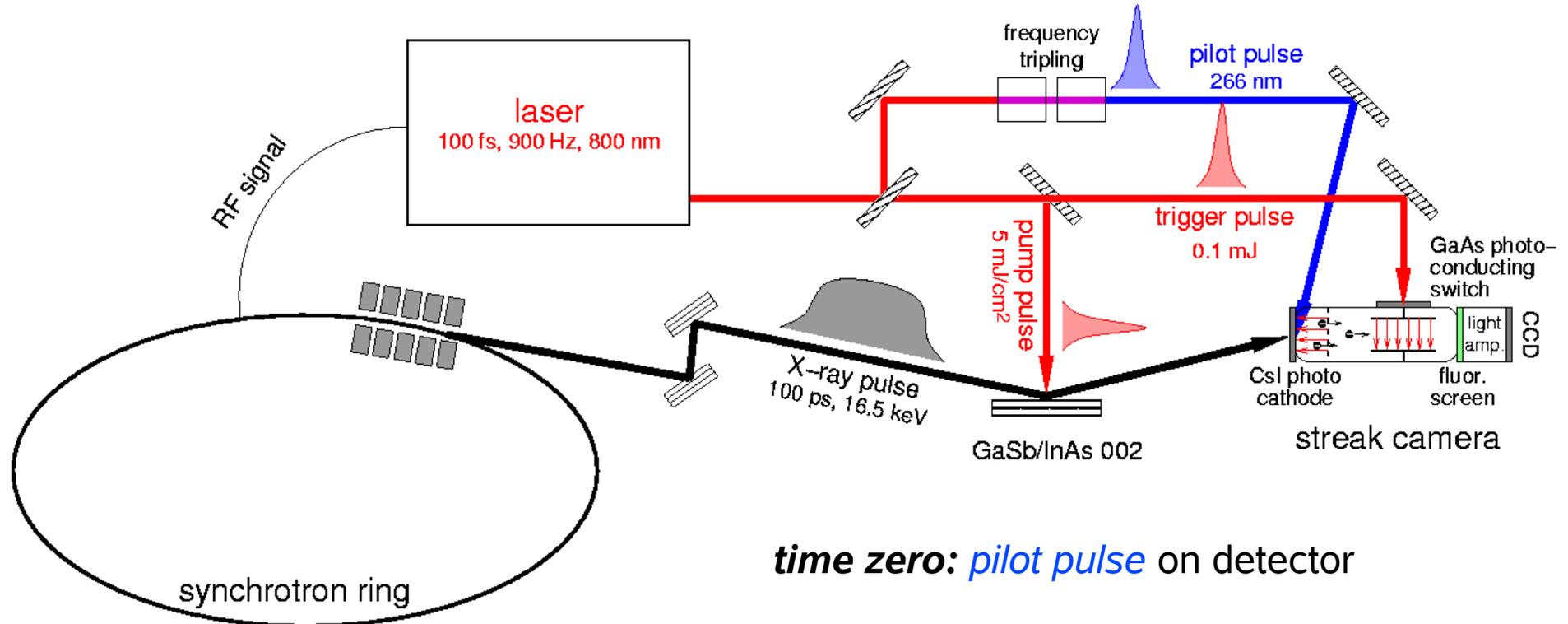


Acoustic waves are partially reflected at each layer interface

phonon dispersion curves are folded into mini-Brillouin zone extra modes

phonons from extra modes should lead to observable "overtones"

TRXD experimental setup

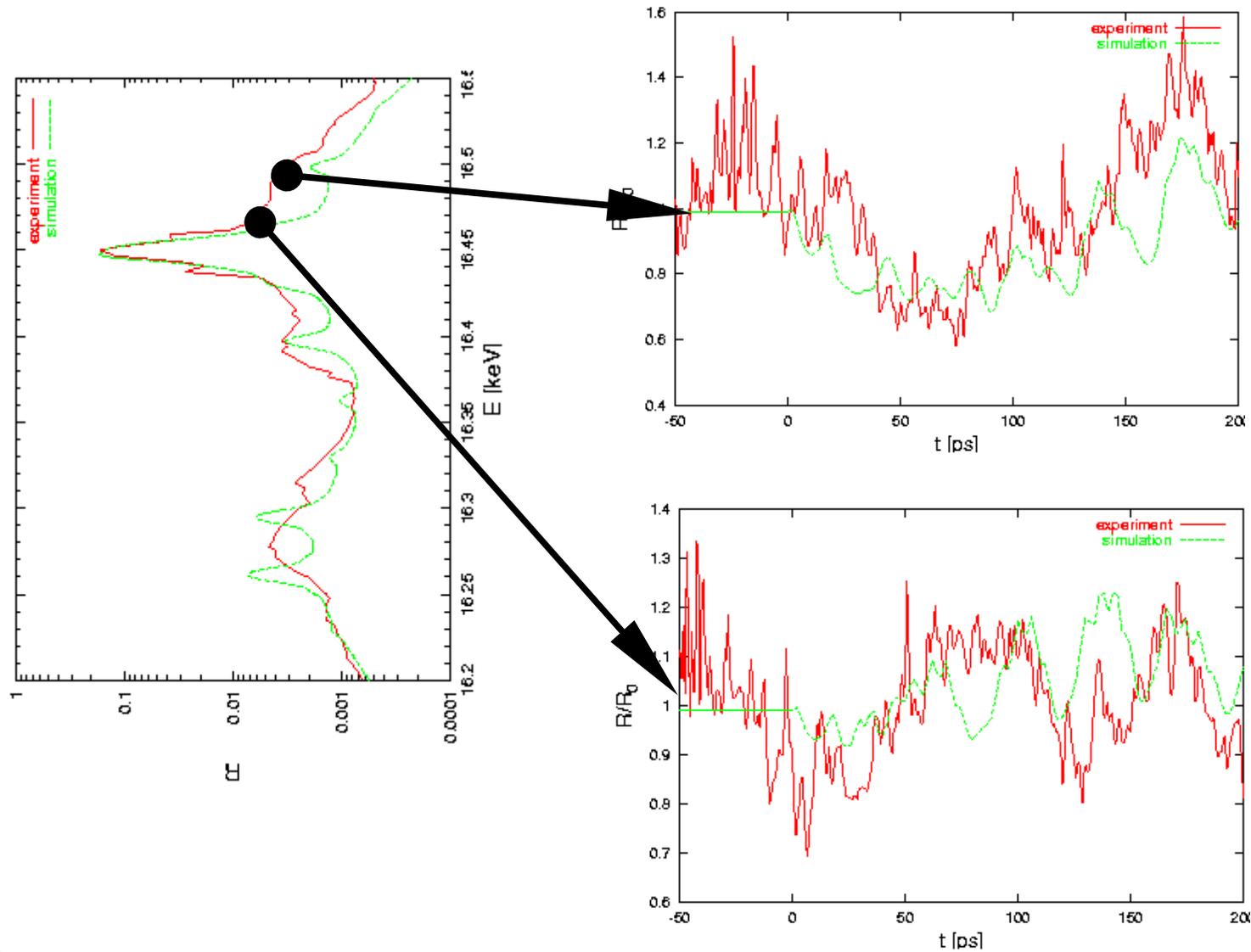


synchronisation:

laser - X-rays: tunable oscillator
cavity length controlled by syn-
chrotron RF signal <10 ps

detector - **laser**: streak camera
triggered by laser via photo-
conducting switch ~4ps

Coherent phonons in the superlattice and reflectivity oscillations



Acoustic phonons and the Takagi-Taupin equation

Takagi-Taupin equation

describes X-ray diffraction from distorted crystals

$$\frac{2i}{k} \frac{\partial D_0}{\partial s_0} = C \bar{\varphi} \chi_{\bar{h}} D_h$$

$$\frac{2i}{k} \frac{\partial D_h}{\partial s_h} = C \varphi \chi_h D_0 - 2\beta_h D_h$$

with:

D_0 : field amplitude incident wave

D_h : field amplitude diffracted wave

C : polarisation factor

χ_h : **Fourier coeff. of susceptibility**

β_h : deviation parameter

$\varphi = \exp(iG_h u)$: **lattice phase**

$u(\mathbf{r}, t)$: distortion field

Takagi-Taupin approximation

susceptibility of distorted crystal approximated by:

$$\chi(\mathbf{r}, t) = \chi^{(p)}(\mathbf{r} - \mathbf{u}(\mathbf{r}, t))$$

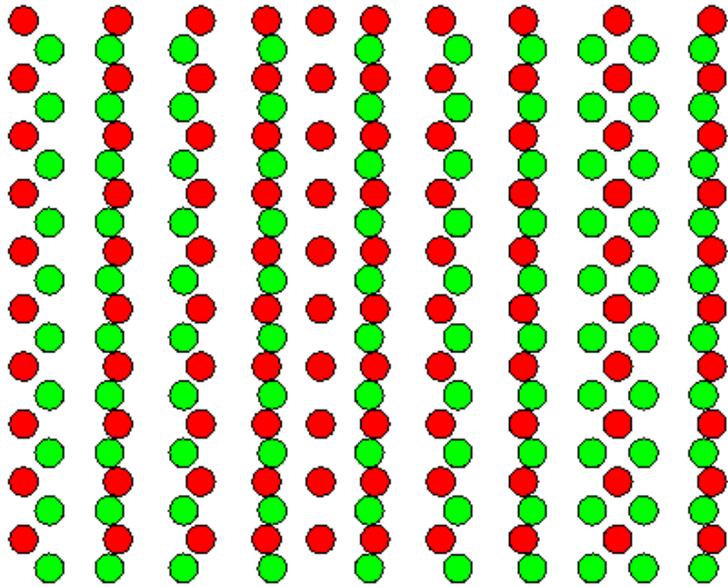
⇒ susceptibilities ($\sim \rho_e$) are shifted as a whole, no deformations

⇒ **only long wavelength acoustic phonons ($\lambda \gg a$) can be described.**

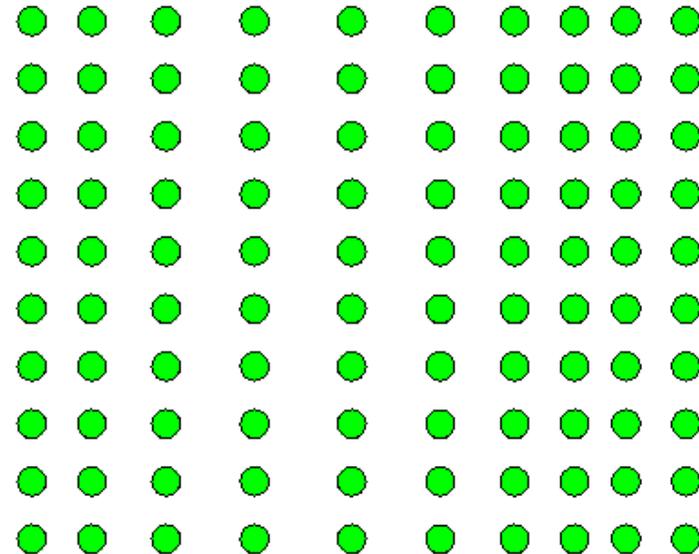
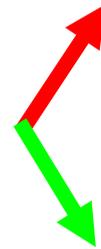
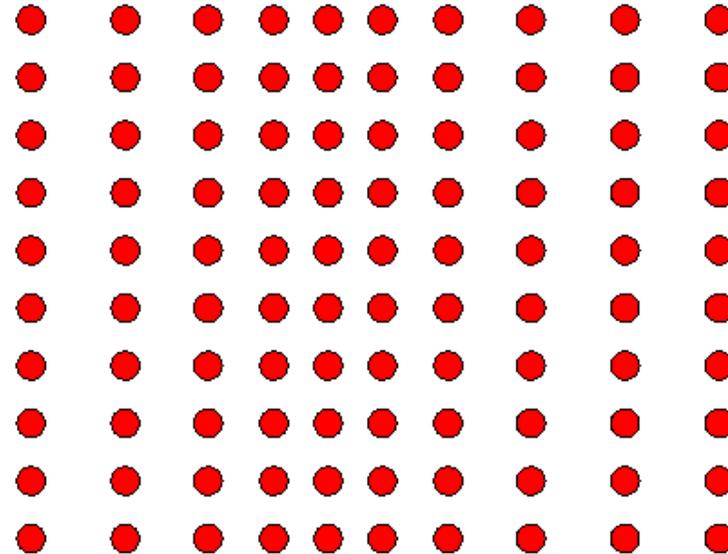
Overcoming the Takagi-Taupin approximation

optical phonon

atoms in a unit cell move relatively to each other \Rightarrow Takagi-Taupin not applicable!



Gedankenexperiment: split up the crystal into 2 "subcrystals" with a primitive basis.
 \Rightarrow optical phonon becomes acoustic in each of these subcrystals!



The generalised Takagi-Taupin equation

Susceptibility of the distorted crystal

The susceptibility is separated into contributions from from each unit-cell atom

$$\chi(\mathbf{r}, t) = \sum_{N=1}^M \chi_N^{(p)}(\mathbf{r})$$

⇒ Allows to assign a different distortion field $\mathbf{u}_N(\mathbf{r}, t)$ to each unit-cell atom:

$$\chi(\mathbf{r}, t) = \sum_{N=1}^M \chi_N^{(p)}(\mathbf{r} - \mathbf{u}_N)$$

Going through the Takagi-Taupin derivation process gives ...

the generalised Takagi-Taupin equation

$$\frac{2i}{k} \frac{\partial D_0}{\partial s_0} = C \tilde{\chi}_{\bar{h}} D_h$$

$$\frac{2i}{k} \frac{\partial D_h}{\partial s_h} = C \tilde{\chi}_h D_0 - 2\beta_h D_h$$

with:

$$\tilde{\chi}_h(\mathbf{r}, t) = \sum_{N=1}^M \chi_{Nh} e^{i\mathbf{G}_h \cdot \mathbf{u}_N(\mathbf{r}, t)}$$

χ_{Nh} : Fourier coefficients of the susceptibility of the perfect primitive subcrystals

Comparison and consistency with "classical" Takagi-Taupin equation

Takagi-Taupin equation

$$\frac{2i}{k} \frac{\partial D_0}{\partial s_0} = C \bar{\varphi} \chi_{\bar{h}} D_h$$

$$\frac{2i}{k} \frac{\partial D_h}{\partial s_h} = C \varphi \chi_h D_0 - 2\beta_h D_h$$

For acoustic phonons

$$\mathbf{u}_1 = \mathbf{u}_2 = \dots = \mathbf{u}_N = \mathbf{u}$$

and thus

$$\tilde{\chi}_h = \varphi \chi_h$$

generalised Takagi-Taupin equation

$$\frac{2i}{k} \frac{\partial D_0}{\partial s_0} = C \tilde{\chi}_{\bar{h}} D_h$$

$$\frac{2i}{k} \frac{\partial D_h}{\partial s_h} = C \tilde{\chi}_h D_0 - 2\beta_h D_h$$

with:

$$\tilde{\chi}_h(\mathbf{r}, t) = \sum_{N=1}^M \chi_{Nh} e^{i\mathbf{G}_h \cdot \mathbf{u}_N(\mathbf{r}, t)}$$

acoustic phonons modulate the phase of χ_h ,
optical phonons also the modulus!

Modelling X-ray diffraction with coherent phonons in quartz

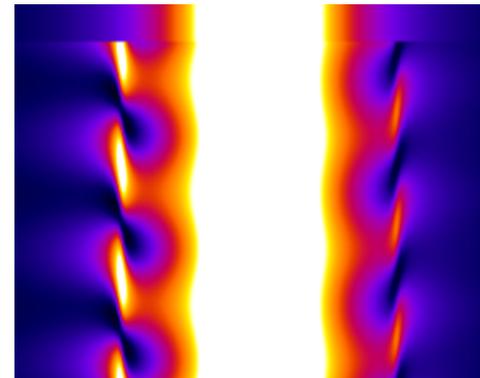
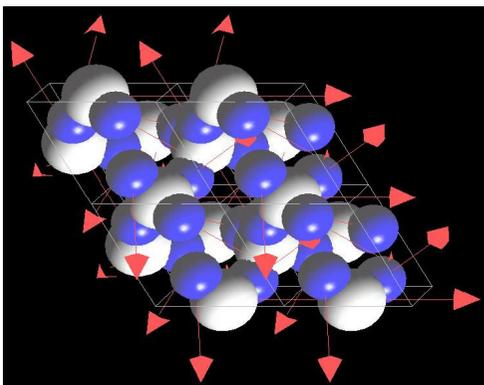
phonons – UNISOFT

- Born von Karman model (springs)
- or explicit interatomic potentials (Born-Meyer, Lennard-Jones, van der Waals, Coulomb)
- shell model (beyond Born approx.)
 - 1) determines dynamical matrix $D(\mathbf{q})$
 - 2) diagonalises $D(\mathbf{q})$
 - \Rightarrow eigen-values Ω_{μ}^2
 - \Rightarrow eigen-vectors $\mathbf{e}_{\mu} \propto \mathbf{u}$

X-ray diffraction – COINS

- gen. Takagi-Taupin equation 1D i.e. for depth dependent distortions only

Solves DE via a variable step size 4th order Runge Cutta algorithm

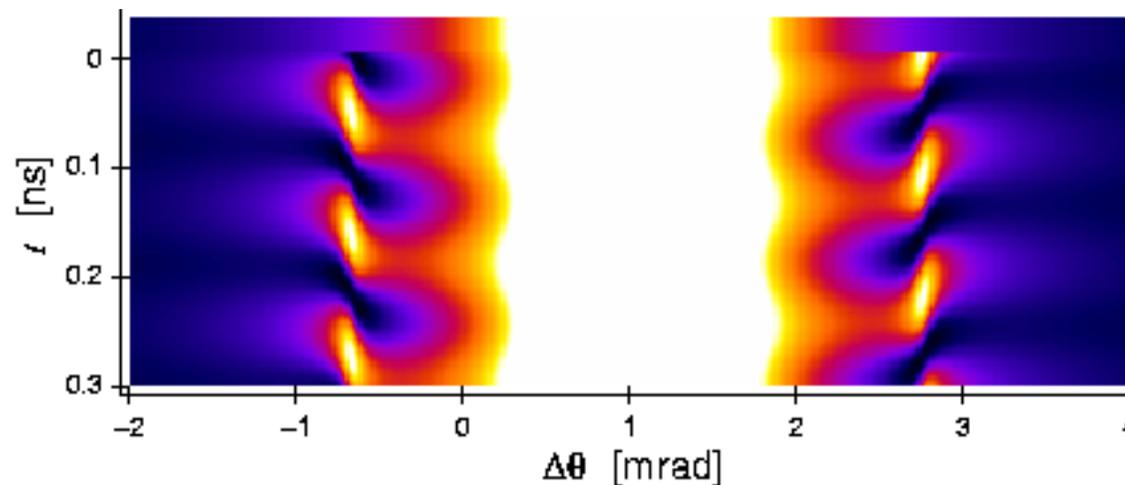


Low frequency acoustic phonons

crystal: α -quartz (010), 30 μm thick, $\phi = 45^\circ$

X-rays: $\lambda = 7.1255 \text{ \AA}$, σ -pol

phonons: A-mode, $q = 1.414 \cdot 10^7 \text{ rad/m}$, $\nu = 9 \text{ GHz}$



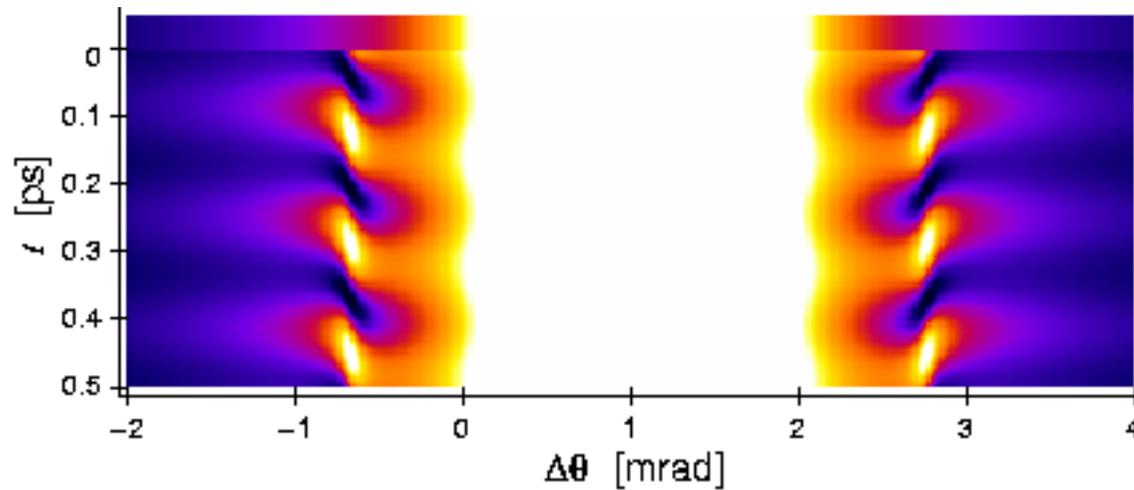
phase difference of π between osc. sidebands

Optical phonons, linearly polarised

crystal: α -quartz (010), 30 μm thick, $\phi = 45^\circ$

X-rays: $\lambda = 7.1255 \text{ \AA}$, σ -pol

phonons: A-mode, $q = 1.414 \cdot 10^7 \text{ rad/m}$, $\nu = 6.03 \text{ THz}$



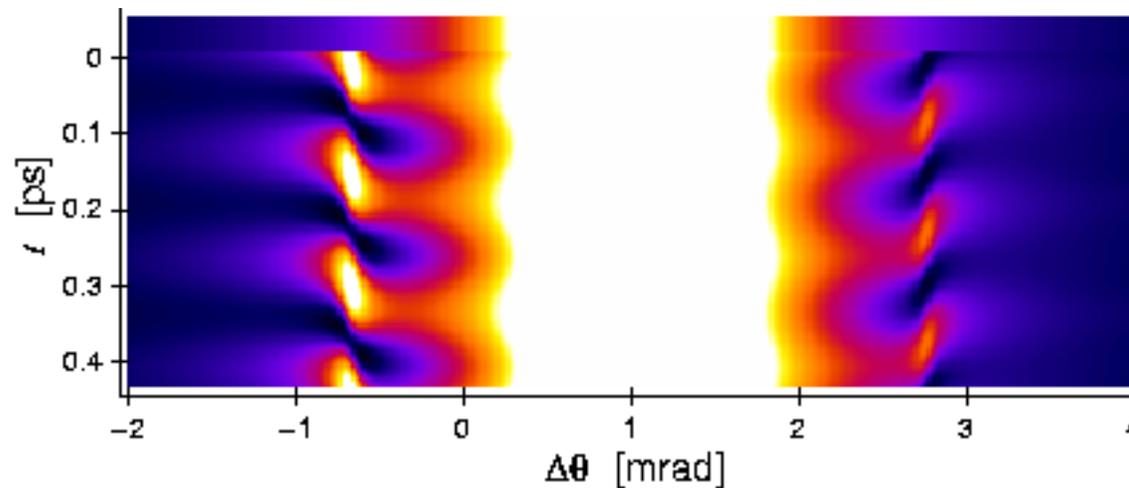
no phase difference between osc. sidebands

Optical phonons, elliptically polarisation

crystal: α -quartz (010), 30 μm thick, $\phi = 45^\circ$

X-rays: $\lambda = 7.1255 \text{ \AA}$, σ -pol

phonons: A-mode, $q = 1.414 \cdot 10^7 \text{ rad/m}$, $\nu = 7.19 \text{ THz}$



phase difference of π between osc. sidebands
sideband amplitudes asymmetric

Perturbative analytical solution of the generalised Takagi-Taupin equation

Small distortion

$$\tilde{\chi}_h(\mathbf{r}, t) = \chi_h + \delta \chi_h(\mathbf{r}, t)$$

⇒ small effect

$$D_h(\mathbf{r}, t) = D_h^{(p)}(\mathbf{r}) + \delta D_h(\mathbf{r}, t)$$

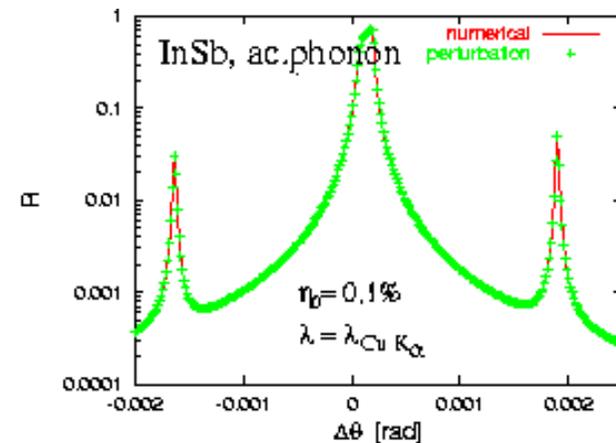
$D_h^{(p)}$: perfect crystal solution

- 1) insert into gen. Takagi-Taupin equation
- 2) neglect terms of the order

$$\delta D_h \delta \chi_h$$

⇒ *resulting equation analytically solvable*

Perturbative solution for phonons excellent for sideband intens. < 10% of rocking curve max. and q not too small



It becomes inaccurate for small q i.e. if sidebands separated from the rocking curve peak by Darwin width or less

Conclusions

- The importance of ultrafast X-ray techniques will increase further with the advent of new short-pulsed high brilliance X-ray sources (FEL, linacs)
- The generalised Takagi-Taupin equation has made a large variety of lattice-dynamical phenomena accessible to TRXD, like:
 - *optical phonons,*
 - *polaritons,*
 - *structural phase transitions ...*
- Different phonon types lead to distinctive features of the rocking curve
 - acoustic phonons
 - ⇒ phase shift π btw. sidebands
 - elliptical polarisation
 - ⇒ asymmetric sidebands
- A perturbative analytical solution of the gen. Takagi-Taupin eqn. has been found
 - 2D
 - very useful to understand the different phenomena